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## INTENSIFICATION OF SINTERING OF CERAMIC TILES USING HIGH-CALCIUM WASTE AND A LITHIUM-BEARING MINERALIZER

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The possibility of using high-calcium waste generated in chemical purification of sewage and lithium-bearing waste in production of ceramic tiles is considered. The processes occurring in their sintering are discussed.

Tiles made of shrinkage-free mixtures have the best parameters in the technology of ceramic facing tiles [1]. Methods for producing such tiles have been developed and proposed in several studies [2, 3]. In particular, introducing an increased quantity of the carbonate component (chalk, lime, dolomite, and other materials) ensures the production of shrinkage-free ceramics in low-temperature firing only in the case of solid-phase sintering of the mixture components. In this case the main requirements imposed on the water absorption and mechanical strength of the product are satisfied. Therefore, in the conditions of fast firing of facing tiles implemented at numerous ceramic works, it is important to develop methods to intensify the process of sintering of low-shrinkage facing tiles.

We have investigated the specifics of the physicochemical processes both in the stage of solid-phase reactions and with the participation of a melt in high-calcium ceramic mixtures, which besides clay and sand contained natural materials (chalk, dolomite, nepheline syenite), waste materials (waste from chemical purification of sewage, cullet), and lithium-bearing waste from chemical fiber production used as a mineralizer.

It was earlier established [4] that lithium-bearing compounds intensify the processes of sintering and phase formation in mixtures with an elevated content of calcium oxide. The ceramic mixtures were prepared using local materials from the Rostov Region: clay from the Vladimirovskoe deposit, sand, and chalk from the Tarasovskoe deposit, as well as high-calcium sewage purification waste from the Rostov power plant and the Novocherkassk power plant, and container glass cullet.

Previous investigations indicated that introduction of lithium-containing compounds (in our case, LiCl) in the amount from 0.3 to 0.4% into a mixture decreases its firing temperature by 100°C. Therefore the firing of the investigated samples was carried out at a temperature of 850–900°C.

Table 1 indicates the main physicochemical parameters of ceramic materials fired within the specified temperature interval based on mixtures that contained:

- mixture 1 — natural calcium-bearing materials (chalk, dolomite, lime, etc.);
- mixture 2 — recycled calcium-bearing materials (waste from chemical purification of sewage);
- mixture 3 — recycled calcium-bearing materials and lithium-bearing waste.

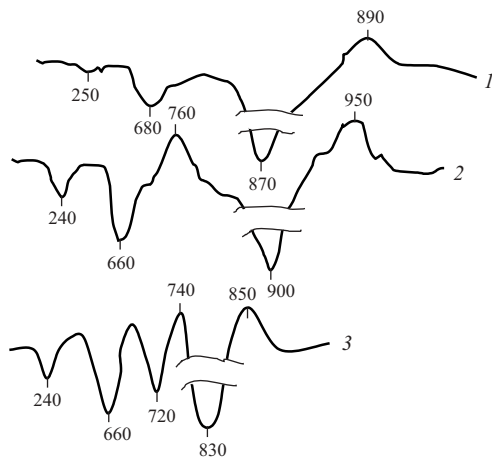
It should be noted that in low-temperature firing (850–900°C) the degree of sintering of the samples nearly satisfied the requirements of GOST 6141–91 with respect to water absorption and mechanical strength, especially samples based on the mixture with the mineralizing additive. However, only the mixture based on the sewage purification waste (mixture 2) can be regarded as low-shrinkage. The mixtures based on natural and recycled materials (mixtures 1 and 2) have a lower mechanical strength than mixture 3, which is presumably due to different processes occurring in materials in low-temperature sintering.

To clarify the specifics of structure formation in ceramic facing tiles using sintering intensifiers, physicochemical studies were carried out. It was revealed in a thermographic analysis that the endothermic effects related to the removal of adsorption water and dehydration of the argillaceous material proceed in all mixtures at virtually the same temperature (Fig. 1). The endothermic effect (mixture 3) at 720°C is presumably due to the formation of a eutectic melt. It is

TABLE 1

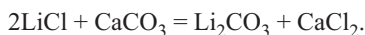
Mixture	Properties after firing		
	shrinkage, %	water absorption, %	compression strength, MPa
1	2.6	15.1	23.0
2	1.2	18.4	21.2
3	1.6	12.2	50.5

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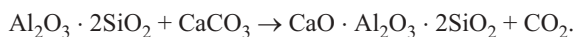


**Fig. 1.** Thermograms of ceramic mixtures. Curve numbers indicate respective mixtures.

known that the melting point of LiCl is equal to 607°C [4]. In this process LiCl actively reacts with calcium carbonate that is not yet decomposed, and low-melting compounds  $\text{Li}_2\text{CO}_3$  and  $\text{CaCl}_2$  are formed with the respective melting points of 618 and 782°C, according to the following mechanism:



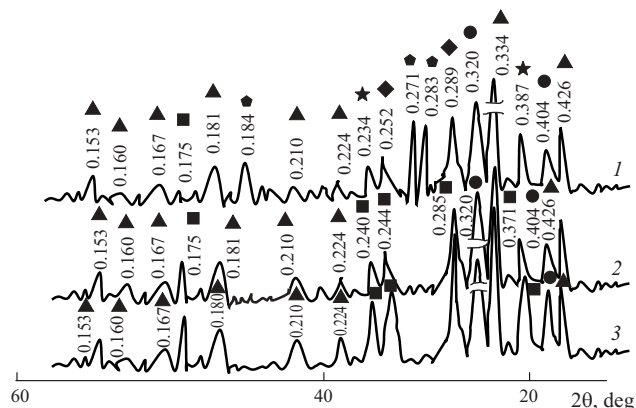
Consequently, the endothermic maximum at 720°C registered on the thermogram is the result of joint melting of the specified compounds. Mixture 2 exhibits a weakly expressed exothermic effect at 760°C, which, according to the data of other analysis methods, in particular, x-ray phase analysis, is related to the formation of anorthite, which is formed at an early stage due to the solid-phase sintering processes in a direct reaction of metakaolinite (the product of clay dehydration) with calcium carbonate according to the following reaction:



This effect is not observed in the mixture based on natural materials. The more defective structure of calcite and the presence of aragonite in the high-calcium waste leads to a higher intensity of the specified reaction, which is corroborated by the intensity of the exothermic effect on the thermogram of mixture 2.

The emergence of a low-melting eutectic in mixture 3 enables this reaction to proceed at a lower temperature (740°C) due to the active effect of the eutectic on the lattice structure of the reactant materials and their increased reaction capacity. The same processes result in earlier decarbonizing of calcite in mixture 3 (830°C).

The exothermic maximum correlating with the crystallization of anorthite formed as a consequence of the reaction between metakaolinite and the product of calcite decomposition registered at 890°C in mixture 1 and at 950°C in mixture 2 is registered as well at a lower temperature (850°C).



**Fig. 2.** X-ray patterns of fired samples: 1 and 2) mixtures 1 and 2 at 1000°C; 3) mixture 3 at 900°C; ▲) quartz; ■) helenite; ♦) diopside; ●) anorthite; ◆)  $2\text{CaO} \cdot \text{SiO}_2$ ; ★) nepheline syenite.

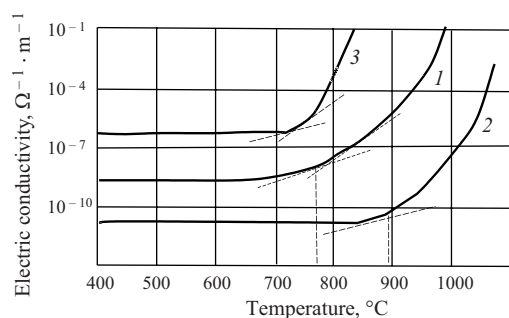
At the same time, according to the x-ray phase analysis data (Fig. 1), the differences in the low-temperature sintering mechanism leads to the formation of other calcium-bearing phases in addition to anorthite: helenite  $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$  and bicalcium silicate  $2\text{CaO} \cdot \text{SiO}_2$ .

Thus, the physicochemical analysis shows that virtually all processes in the mixture containing the LiCl additive occur at lower temperatures. The effect of LiCl as the strongest mineralizer on the high-calcium mixtures is due not only to its melting at 607°C but by the possibility of its forming a complex flux with a series of low-melting eutectics.

In fact the study of the curves representing a relative modification of electric conductivity (Fig. 3) shows an abrupt increase in the conductivity in mixture 3 already at a temperature of 720°C, which points to the emergence of a micromelt and the sintering process proceeding in the liquid-phase state. Mixtures 1 and 2 exhibit a significant change in the conductivity at higher temperatures: 790 and 830°C, respectively, i.e., the liquid-phase process in them starts at these temperatures.

Consequently the main factor intensifying the sintering of high-calcium ceramic mixtures is the significant intensifying effect of LiCl, which results in the formation of low-temperature eutectics and, accordingly, in an earlier formation of the micromelt. Furthermore, the introduction of lithium-bearing additives in a ceramic mixture facilitates an abrupt decrease in the viscosity of the micromelt [5]. The products of the solid-phase transformations in this case are in direct contact with the liquid phase, which also contributes to intensifying the firing process.

Thus, the formation of ceramics takes place both as the result of solid-phase chemical processes and with participation of the liquid phase in the form of a micromelt. It is known that the main crystalline phases are formed more intensely after the emergence of the micromelt. This agrees well with the data of x-ray phase analysis (see Fig. 2). Thus, the following crystalline phases were identified in the sample



**Fig. 3.** Variation in electric conductivity depending on temperature. Curve numbers indicate respective mixtures.

of mixture 1 fired at 1000°C: quartz (0.426, 0.334, 0.221, and 0.167 nm), nepheline syenite (0.387, 0.289, 0.234 nm),  $2\text{CaO} \cdot \text{SiO}_2$  (0.271, 0.286, 0.297 nm), diopside  $\text{CaMg}(\text{SiO}_3)_2$  (0.298, 0.283, 0.252 nm), and anorthite (0.313, 0.320, 0.404 nm). This differs significantly from the phase composition of mixture 2 containing high-calcium waste, in which the following phases were identified: quartz (0.426, 0.334, 0.221, 0.167 nm), anorthite (0.251, 0.300, 0.320, 0.404 nm), and helenite (0.175, 0.240, 0.244, 0.285, and 0.371 nm).

Anorthite is formed in sample 2 in the stage of solid-phase sintering, which, in our opinion, impedes the formation of bicalcium silicate in the presence of the micromelt at elevated temperatures due to an insufficient quantity of  $\text{CaO}$ , since the calcium-bearing components react with metakaolinite and form aluminosilicates already in the state of solid-phase reaction. This has a positive effect on the service properties of the tiles, since bicalcium silicate becomes hydrated in service, which leads to the destruction of the article.

A 0.4% additive of the lithium-containing waste to mixture 2 fired at 900°C does not qualitatively modify the phase composition of the resulting material. The phase and struc-

ture formation in ceramics is fully completed at this sintering temperature, which is corroborated by the x-ray phase analysis data (see Fig. 2): the diffraction maxima typical of anorthite and helenite are more clearly expressed.

The studies performed determined the dependences of the structure formation process in ceramic facing tiles based on mixtures using high-calcium sewage purification waste and lithium-bearing sintering mineralizer. It is established that anorthite  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  is formed in the reaction of metakaolinite (the product of dehydration of the clay material) directly with  $\text{CaCO}_3$  in the stage of the solid-phase processes at 700–800°C, and helenite arises at higher temperatures along with anorthite in the reaction with  $\text{CaO}$ . The sintering mechanism with the participation of the lithium-bearing waste is clarified. This waste is a strong mineralizer not only due to its melting at 607°C, but also due to the fact that it forms a series of low-melting eutectics, which ensures the completion of the ceramic structure formation at a temperature below 900°C.

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